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(54) Modified block copolymers and process for the preparation thereof

(57) A block copolymer comprises a monoalkenylaromatic hydrocarbon block and a hydrogenated conjugated diene hydrocarbon block in which groups  $-N(H)-S(O)(O)R$ , R being an organic radical, are grafted at the aromatic groups. The copolymer is prepared by reacting the block copolymer with an azide  $R(O)(O)S-N_3$ , e.g. 3-azidosulphonylbenzoic acid. The radical R is preferably aromatic, e.g. 3-carboxyphenyl. Prior to modification, the copolymer is especially of styrene and butadiene, and is e.g. of ABA form, where A is styrene.

GB 2 205 103 /

MODIFIED BLOCK COPOLYMERS AND PROCESS  
FOR THE PREPARATION THEREOF

The invention relates to a functionalized, selectively hydrogenated block copolymer comprising at least one block A being predominantly a polymerized monoalkenylaromatic hydrocarbon block and at least one block B being, prior to hydrogenation, predominantly a polymerized conjugated diene hydrocarbon block, of which block B  
5 the unsaturation has been reduced by hydrogenation to less than 10% of the original unsaturation and of which block A the unsaturation is above 50% of the original unsaturation. The invention also relates to a process for the preparation of such functionalized,  
10 selectively hydrogenated block copolymers.

Block copolymers can be obtained by anionic copolymerization of a conjugated diene and a monoalkenylaromatic hydrocarbon by using an organic alkali metal initiator. These types of block copolymers are diversified in characteristics, ranging from rubber-  
15 like characteristics to resin-like characteristics, depending on the content of monoalkenylaromatic compound.

When the content of monoalkenylaromatic compound is small, the produced block copolymer is a so-called thermoplastic rubber. It is a very useful polymer which shows elasticity in the unvulcanized  
20 state and is applicable for various uses such as mouldings of shoe sole, impact modifier for polystyrene resins, adhesives and binders.

The block copolymers with a high content of monoalkenylaromatic compound, such as more than 70% by weight, provide a resin possessing both excellent impact resistance and transparency, and such resins  
25 are widely used for packaging.

The elastomeric properties of block copolymers also appear to be due in part to their degree of branching. While the polymers of monovinylaromatic hydrocarbons have a basic straight carbon chain backbone, those with elastomeric properties always have pending

alkyl radicals. For example, ethylene-propylene rubber has a structure of pending methyl radicals which appears to provide elasticity and other elastomeric properties, such as high elongation and high tensile strength.

5       Block copolymers have been produced, see U.S. patent specification Re 27,145 which comprise primarily those having the general structure A-B-A wherein the two terminal polymer blocks A comprise thermoplastic polymer blocks of vinylarenes, such as polystyrene, while block B is a polymer block of a selectively  
10       hydrogenated conjugated diene. The proportion of the thermoplastic terminal blocks to the centre elastomeric polymer block and the relative molecular weights of each of these blocks is balanced to obtain a rubber having an optimum combination of properties such that it behaves as a vulcanized rubber without requiring the actual  
15       step of vulcanization. Moreover, these block copolymers can be designed not only with this important advantage but also so as to be handled in thermoplastic forming equipment and are soluble in a variety of relatively low cost solvents.

      The selective hydrogenation has rendered the block copolymers  
20       less sensitive to oxidation and may be effected selectively as disclosed in US patent specification Re 27,145. These polymers are hydrogenated block copolymers having a configuration, prior to hydrogenation of A-B-A wherein each of the A blocks is an alkenyl-substituted aromatic hydrocarbon polymer block and B is a butadiene  
25       polymer block wherein 35-55 mol per cent of the condensed butadiene units in the butadiene polymer block have 1,2-configuration.

      These selectively hydrogenated ABA block copolymers are deficient in many applications in which adhesion is required due to its hydrocarbon nature. Examples include the toughening and  
30       compatibilization of polar polymers such as the engineering thermoplastics, the adhesion to high energy substrates of hydrogenated block copolymer elastomer based adhesives, sealants and coatings, and the use of hydrogenated elastomer in reinforced polymer systems. However, the placement onto the block copolymer of functional  
35       groups which can provide interactions not possible with hydrocarbon

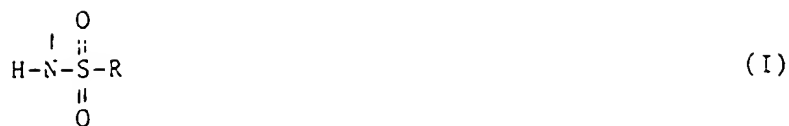
polymers solves the adhesion problem and extends the range of applicability of this material.

Beyond the very dramatic improvement in interface adhesion in polymer blends, a functionalized S-EB-S component can also contribute substantially to the external adhesion characteristics often needed in polymer systems. "EB" refers to "ethylene-butylene". These include adhesion to fibres and fillers which reinforce the polymer system; adhesion to substrates in adhesives, sealants, and coatings based on functionalized S-EB-S polymers, adhesion of decorations such as printing inks, paints, primers, and metals of systems based on S-EB-S polymers; participation in chemical reactions such as binding proteins such as heparin for blood compatibility; surfactants in polar-non-polar aqueous or non-aqueous dispersions.

Functionalized S-EB-S polymer can be described as basically commercially produced S-EB-S polymers which are produced by hydrogenation of styrene-butadiene-styrene (S-B-S) block copolymer to which is chemically attached to either the styrene or the ethylene-butylene block, chemically functional moieties.

Functionalized, selectively hydrogenated block copolymers of the type described hereinbefore have now been found which, compared with the corresponding non-functionalized selectively hydrogenated block copolymers have a higher tensile strength and a higher elongation at break, both in particular at elevated temperature; moreover, they show the improvements described hereinbefore with respect to the known functionalized, selectively hydrogenated block copolymers.

Accordingly, the invention provides a functionalized, selectively hydrogenated block copolymer comprising at least one block A being predominantly a polymerized monoalkenylaromatic hydrocarbon block and at least one block B being, prior to hydrogenation, predominantly a polymerized conjugated diene hydrocarbon block, of which block B the unsaturation has been reduced by hydrogenation to less than 10% of the original unsaturation and of which block A the unsaturation is above 50% of the original unsaturation, in which groups of the general formula I



in which R represents an organic radical, are grafted at aromatic groups in the blocks A.

Block copolymers of conjugated dienes and vinylaromatic hydrocarbons which may be utilized include any of those which exhibit elastomeric properties and those which have 1,2-micro-structure contents prior to hydrogenation of from 7% to 100%. Such block copolymers may be multiblock copolymers of varying structures containing various ratios of conjugated dienes to monoalkenylaromatic hydrocarbons including those containing up to 60 per cent by weight of monoalkenylaromatic hydrocarbon. Thus, multiblock copolymers may be utilized which are linear or radial, symmetric or asymmetric and which have structures represented by the formulae A-B, A-B-A, A-B-A-B, B-A, B-A-B, B-A-B-A, (AB)<sub>0,1,2...</sub>BA and the like wherein A is a polymer block of a monoalkenylaromatic hydrocarbon or a conjugated diene/monoalkenylaromatic hydrocarbon tapered copolymer block and B is a polymer block of a conjugated diene. The block copolymer preferably has the general formula B<sub>n</sub>(AB)<sub>o</sub>A<sub>p</sub> wherein n = 0 or 1, o = 0 or an integer of at least 1 and p = 0 or 1, in which not more than one of n, o or p are equal to zero. Particularly preferred are block copolymers having at least one mid block B and at least two end blocks A. Diblock copolymers AB are also very suitable. Suitably, the blocks A comprise 5 to 95 per cent by weight, preferably 5 to 35 per cent and particularly 5 to 30 percent by weight of the block copolymer.

The block copolymers may be produced by any well-known block polymerization or copolymerization procedures including the well-known sequential addition of monomer techniques, incremental addition of monomer technique or coupling technique as illustrated in, for example, U.S. patent specifications 3,251,905; 3,390,207; 3,598,887 and 4,219,627. As is well known in the block copolymer art, tapered copolymer blocks can be incorporated in the multiblock copolymer by copolymerizing a mixture of conjugated diene and alkenylaromatic hydrocarbon monomers utilizing the difference in

their copolymerization reactivity rates. The tapered copolymer blocks contain predominantly one polymer, for example greater than 85%. Various patent specifications describe the preparation of multiblock copolymers containing tapered copolymer blocks including U.S. patent specifications 3,251,905; 3,265,765; 3,639,521 and 4,208,356.

Conjugated dienes which may be utilized to prepare the polymers and copolymers are those having from 4 to 8 carbon atoms per molecule and include, for example, 1,3-butadiene, 2-methyl-1,3-butadiene(isoprene), 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene and 1,3-hexadiene. Mixtures of such conjugated dienes may also be used. The preferred conjugated diene is 1,3-butadiene.

Alkenylaromatic hydrocarbons which may be utilized to prepare copolymers include vinylaromatic hydrocarbons, such as styrene, o-methylstyrene, p-methylstyrene, p-tert-butylstyrene, 1,3-dimethylstyrene, alpha-methylstyrene, vinylnaphthalene and vinylanthracene. The preferred vinylaromatic hydrocarbon is styrene.

According to a preferred embodiment of the present invention the block copolymer is a styrene-butadiene-styrene block copolymer. The polymerized styrene blocks preferably have an average molecular weight between 2,000 and 115,000, particularly between 4,000 and 60,000 and the polymerized butadiene blocks preferably have an average molecular weight between 20,000 and 450,000, particularly between 35,000 and 150,000. Suitably, in the range from 35 to 55 mol% and preferably 40 to 50 mol% of the condensed butadiene units in block B have a 1,2-configuration. Preferably, an average of less than 25% and more preferably less than 10% of the blocks A are hydrogenated. The average unsaturation of the hydrogenated block copolymer has suitably been reduced to less than 20% of its original value.

It should be observed that the above-described polymers and copolymers may, if desired, be readily prepared by the methods set forth hereinbefore. However, since many of these polymers and copolymers are commercially available, it is usually preferred to

employ the commercially available polymer as this serves to reduce the number of processing steps involved in the overall process. The hydrogenation of these polymers and copolymers may be carried out by a variety of well-established processes including hydrogenation in the presence of such catalysts as Raney Nickel, noble metals of Group 8 of the Periodic Table of the Elements, such as platinum and palladium, and soluble transition metal catalysts. Suitable hydrogenation processes which can be used are ones wherein the diene-containing polymer or copolymer is dissolved in an inert hydrocarbon diluent such as cyclohexane and hydrogenated by reaction with hydrogen in the presence of a soluble hydrogenation catalyst. Such processes are disclosed in U.S. Patent Specifications 3,113,986 and 4,226,952. The polymers and copolymers are hydrogenated in such a manner as to produce hydrogenated polymers and copolymers having a residual unsaturation content in the polydiene block of from 0.5 to 10 per cent, and preferably less than 5 per cent of their original unsaturation content prior to hydrogenation.

The organic radical represented by R in the general formula I is preferably an aromatic group and, more preferably, a phenyl group. Other examples of groups R are naphthyl and anthryl groups. R may further represent a cycloalkyl group, for example a cyclobutyl, cyclopentyl or cyclohexyl group, or an alkyl group, for example a pentyl, hexyl, heptyl, octyl, nonyl or decyl group. According to a preferred embodiment of the present invention R represents an organic radical containing a carboxyl group, in particular a 3-carboxyphenyl or a 4-carboxyphenyl group; very good results have been obtained with 3-carboxyphenyl groups.

The organic radical R in the general formula I may contain substituents other than carboxyl groups, either in the presence or in the absence of carboxyl groups. Examples of such substituents are halogen atoms, i.e. fluorine, chlorine, bromine or iodine atoms; cyano groups; hydroxyl groups; dialkylamino groups; nitro groups or benzoyl groups. Aromatic groups represented by R may carry, for example, an alkyl or a cycloalkyl group and alkyl groups represented by R may carry, for example, an aromatic or a cycloalkyl



group. It is not excluded that R represents a heterocyclic group, for example a 2-thienyl, a 3-thienyl, a 2-furyl, a 3-furyl, a 2-pyridyl, a 3-pyridyl or a 4-pyridyl group or a group obtained by hydrogenation of each of these seven groups. Specific examples of groups R are 3-carboxy-4 hydroxyphenyl, 3-carboxy-4 chlorophenyl, 4-(carboxymethoxy)phenyl, 3,4-dicarboxyphenyl, 5-carboxynaphthyl, 2-neopentyl-5-carboxyphenyl and 2-ethyl-5-carboxyphenyl groups.

The invention further provides a process for the preparation of a functionalized, selectively hydrogenated block copolymer as described hereinbefore which process comprises reacting a selectively hydrogenated block copolymer comprising at least one block A being predominantly a polymerized monoalkenylaromatic hydrocarbon block and at least one block B being, prior to hydrogenation, predominantly a polymerized conjugated diene hydrocarbon block, of which block B the unsaturation has been reduced by hydrogenation to less than 10% of the original unsaturation and of which block A the unsaturation is above 50% of the original unsaturation, with an azide having the general formula II



in which R has the same meaning as in the general formula I.

It has, surprisingly, been found that the process according to the present invention results in grafting of the groups of the general formula I selectively to the aromatic groups in the blocks A.

The process according to the present invention is preferably carried out by heating an admixture of the selectively hydrogenated block copolymer and an azide of the general formula II to a temperature in the range of from 100 °C to 300 °C and particularly from 150 °C to 250 °C.

The azide of the general formula II may be admixed with the block copolymer in any suitable manner, for example in a powder mixer or, in a melt on a conventional rubber mill, or in an internal mixer, or in an extruder such as a Brabender mixer.

In addition to the azide, other ingredients can also be incorporated, for example fillers, extenders, pigments, stabilizers and plasticizers. If desired, the process according to the present invention may be carried out in the presence of a radical scavenger to prevent any degradation of aliphatic carbon carbon bonds in the block copolymer. Examples of radical scavengers are sterically hindered phenols such as "Ionox 220", a trade mark for 4,4'-methylene-bis-2,6-ditertiary butylphenol and "Ionox 330", a trade mark for 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene.

The following Examples further illustrate the invention. The experiments were carried out with Kraton G 1652 which is a trade mark for a selectively hydrogenated block copolymer ABA in which "A" is a styrene block having an average molecular weight of about 7500 and "B" is a hydrogenated polybutadiene block having an average molecular weight of about 37,000 and having an unsaturation of less than 5% of its original value.

#### Example 1

A mixture of powdered Kraton G 1652 (50 g) and 3-azidosulphonylbenzoic acid (2 g) was fed to a Brabender mixer provided with kneading screws and having a temperature of 190 °C at the start and 210 °C at the end of the reaction. The mixer was used at a speed of 30 revolutions per min (rpm). The styrene blocks and the ethylene-butylene blocks in the Kraton G 1652 had a molecular weight of 7,500 and 37,000, respectively. The residence time of the material in the mixer was 5 min. NMR analysis showed that 80% of the 3-azidosulphonyl-benzoic acid was grafted to the block copolymer and that 80% thereof was grafted to the aromatic groups.

The material withdrawn from the mixer was allowed to adopt ambient temperature and was subsequently heated for 15 min in a mould at 185 °C to prepare test sheets having dimensions of 11.5x11.5x0.1 cm and wherefrom test specimen having dimensions according to DIN 53,504, type S3A were prepared. The tensile strength and elongation at break at 23 °C and 70 °C and moduli at

70 °C were determined according to method ISO R527, using a strain rate of 200 mm per min. These properties were also determined for the starting Kraton G 1652. The table hereinafter presents the results.

TABLE

	Tensile Strength, MPa		Elongation at break, %		Modulus at 70 °C, MPa, at	
	23 °C	70 °C	23 °C	70 °C	300%	500%
Kraton G 1652	31.0	3.2	500	525	2.6	3.1
Modified Kraton G 1652	35.0	4.2	617	750	2.9	3.7

5 The table shows that the process according to the invention had resulted in an increase of the tensile strength at 23 °C and at 70 °C of 13% and 31%, respectively, and in an increase of elongation at break at 23 °C and at 70 °C of 23% and 43%, respectively.

Example 2

10 Powdered Kraton G 1652 (50 g) was heated in the Brabender mixer, at a speed of 30 rpm, to a temperature of 145 °C and at this temperature 3-azidosulphonylbenzoic acid (2 g) was added. The temperature of the mixture thus obtained was increased to 190 °C in a period of 3 min and then increased from 190 °C to 210 °C in four

15 min.  
The material withdrawn from the mixer was allowed to adopt ambient temperature and was subsequently heated for 15 min in a mould at 185 °C to prepare test sheets. The tensile strength, the elongation at break and the moduli at 70 °C were the same as those  
20 of the modified Kraton G 1652 in the Table hereinbefore.

C L A I M S

1. A functionalized, selectively hydrogenated block copolymer comprising at least one block A being predominantly a polymerized monoalkenylaromatic hydrocarbon block and at least one block B being, prior to hydrogenation, predominantly a polymerized conjugated diene hydrocarbon block, of which block B the unsaturation has been reduced by hydrogenation to less than 10% of the original unsaturation and of which block A the unsaturation is above 50% of the original unsaturation, in which groups of the general formula I



- in which R represents an organic radical, are grafted at aromatic groups in the blocks A.
2. A block copolymer as claimed in claim 1 in which the blocks A have an average molecular weight in the range of from 2,000 to 115,000 and blocks B from 20,000 to 450,000.
3. A block copolymer as claimed in claim 1 or 2 which has at least one mid block B and at least two end blocks A.
4. A block copolymer as claimed in any one of the preceding claims in which the blocks A comprise in the range of from 5 to 35% by weight of the block copolymer and the unsaturation of block B has been reduced to less than 5% of its original value.
5. A block copolymer as claimed in any one of the preceding claims in which block A is a polystyrene block and block B, prior to hydrogenation, is a polybutadiene block.
6. A block copolymer as claimed in any one of the preceding claims in which R in the general formula I represents an aromatic group.
7. A block copolymer as claimed in claim 6 in which R in the general formula I represents an optionally substituted phenyl group.

8. A block copolymer as claimed in claim 7 in which R in the general formula I represents a 3-carboxyphenyl group.

9. A block copolymer as claimed in any one of the preceding claims in which the groups of the general formula I are present in an amount in the range of from 0.1 to 20% by weight, calculated on the functionalized, selectively hydrogenated block copolymer.

10. A block copolymer substantially as hereinbefore described with reference to the Examples.

11. A process for the preparation of a functionalized, selectively hydrogenated block copolymer as claimed in any one of the preceding claims which process comprises reacting a selectively hydrogenated block copolymer comprising at least one block A being predominantly a polymerized monoalkenyl aromatic hydrocarbon block and at least one block B being, prior to hydrogenation, predominantly a polymerized conjugated diene hydrocarbon block, of which block B the unsaturation has been reduced by hydrogenation to less than 10% of the original unsaturation and of which block A the unsaturation is above 50% of the original unsaturation, with an azide having the general formula II



in which R has the same meaning as in the general formula I.

12. A process as claimed in claim 11 which is carried out at a temperature in the range of from 100 °C to 300 °C.

13. A process as claimed in claim 11 substantially as hereinbefore described with reference to the Examples.